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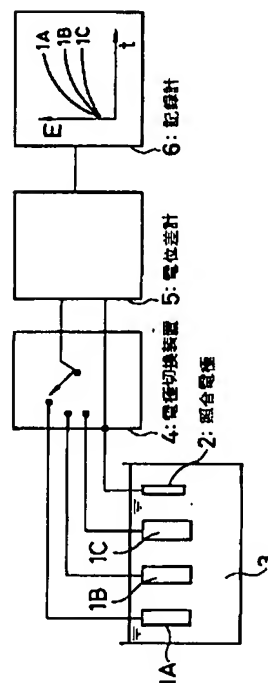
(54) 【発明の名称】 耐腐食性の試験方法

(57) 【要約】

【目的】 微生物が関与する銅管の孔食を、小容量の試験水で、短時間で容易に、適正に評価する。

【構成】 活性酸素発生源と酸化還元色素を含む水3中に金属試料電極1A~1Cと照合電極2を浸漬し、両電極間の電位差を測定する。

【効果】 少量の活性酸素を発生する実際の微生物反応による腐食を模擬すべく、活性酸素発生源により水中で微量の活性酸素を発生させると共に、酸化還元色素を電子メディエータとして反応に介在させ、金属試料電極から電子を引き抜き易い環境とした試験水中に、金属試料電極と照合電極とを浸漬し、両電極間の自然電位の変化を測定する。金属試料電極の耐腐食性を、加速された電位変化として、迅速かつ適正に評価することができる。



【特許請求の範囲】

【請求項1】 活性酸素発生源と酸化還元色素とを含む水中に金属試料電極と照合電極とを浸漬し、両電極間の電位差を測定することを特徴とする耐腐食性の試験方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は耐腐食性の試験方法に係り、特に、熱交換器用ないし配管用金属材料の腐食、とりわけ微生物が関与する銅管の孔食を簡単な装置で迅速かつ適正に評価する耐腐食性の試験方法に関する。

【0002】

【従来の技術】配管や熱交換器などに用いられている配管において局部腐食が進行して孔食深さが増し、それが貫通に至るとプラントの操業停止など不測の事態を生ずることがあるため、局部腐食、即ち孔食の発生を予知する技術が求められている。

【0003】従来、熱交換器又は配管の孔食の発生は、当該設備の運転、通水を休止してその一部をサンプリングし、サンプルの孔食状況を調べることにより予知していた。

【0004】しかしながら、このような方法では、設備の運転を休止し、かつその一部をサンプリングするために破壊しなければならないことから、工場の操業に影響を及ぼすという欠点がある。しかも、測定結果が出るまでに多大の時間、労力、費用がかかるという欠点もある。

【0005】このような欠点を解決するものとして、配管の孔食の進行状況をモニターする方法がある。即ち、例えば、実機水系内又は実機水系から採取した水中に、モニタリングする配管と同一材質からなるテストピースを浸し、このテストピースと比較電極との間の電位差の経時変化を測定することにより、孔食状況をモニターする。この方法は、配管に孔食が発生する前段階として管材の自然電位が上昇するという現象を利用するものであり、このような方法によれば、設備の運転を休止することなく、非破壊にて孔食を推定することが可能とされる。

【0006】一方、1994年5月25日発行の「腐食防食シンポジウム要旨集」第129頁～第132頁には、グルコースを酸化酵素で分解して過酸化水素(H_2O_2)を発生させ、 H_2O_2 が鋼材から電子を受けとって H_2O になる反応を利用して鋼材の耐微生物腐食試験を行う方法が提案されている。

【0007】

【発明が解決しようとする課題】前述の管材の自然電位の上昇現象を利用して、テストピースを用いて孔食の進行状況をモニターする方法では、実機水系内又は実機水系から多量(約100リットル)に採取した水の中に、テストピースを浸漬してその電位の経日変化を測定する

必要がある。この方法で電位上昇の有無を判断するためには、約1ヶ月の経日測定が必要とされるため、数時間といった短時間で、しかも、小容量の試験水で評価を行うことはできないという欠点がある。

【0008】一方、「腐食防食シンポジウム要旨集」に記載される鋼材の耐微生物腐食試験方法では、次のような問題点がある。即ち、多量の H_2O_2 を発生させる加速テストであるため、高濃度の H_2O_2 が直接鋼材に作用して電位上昇をもたらす。このような系では、試験環境が過激すぎて、長期にわたって徐々に反応が進行する(但し、一旦反応が始まるとその後の進行は速い。)微生物腐食反応の模擬試験としては問題が残る。

【0009】本発明は上記従来の問題点を解決し、熱交換器用ないし配管用金属材料の腐食、特に微生物が関与する銅管の孔食を、小容量の試験水により、短時間で容易に、しかも、適正に評価することができる耐腐食性の試験方法を提供することを目的とする。

【0010】

【課題を解決するための手段】本発明の耐腐食性の試験方法は、活性酸素発生源と酸化還元色素とを含む水中に金属試料電極と照合電極とを浸漬し、両電極間の電位差を測定することを特徴とする。

【0011】以下に本発明を図面を参照して詳細に説明する。

【0012】図1は本発明の耐腐食性の試験方法の実施に好適な試験装置の一実施例を示す系統図であり、図中、1A、1B、1Cは金属試料電極、2は照合電極であり、活性酸素発生源と酸化還元色素とを含む水(以下「試験水」と称する場合がある。)3中に浸漬されると共に、これら金属試料電極1A、1B、1Cと照合電極2との間の電位差を測定するための電位差計5が電極切換装置4を介して接続されている。また、この電位差計5の測定結果を表示する記録計6が設けられている。

【0013】本発明において、活性酸素発生源としては、水中で自動酸化反応により活性酸素を発生し易く、しかも、容易に入手可能なキシロース(xylose)が好適に用いられるが、何らこれに限定されるものではない。

【0014】一方、酸化還元色素としては、NBT(Nitro Blue Tetrazolium: $C_{40}H_{30}N_{10}O_6$ Cl_2 =分子量817.65)が好適である。

【0015】これら活性酸素発生源及び酸化還元色素は、一定温度、好ましくは20℃以上、特に好ましくは30℃以上に維持された水に添加されて試験に供されるが、この水としては、電位差の測定値の上昇を顕著なものとすることができることから、リン酸又はリン酸塩を含むリン酸緩衝液を用いるのが好ましく、特に、リン濃度100ppm以上、とりわけ100～1000ppmの中性ないし微アルカリ性、即ち、pH6～9程度のリン酸緩衝液が好適である。

【0016】このようなリン酸緩衝液中のNBT等の酸

化還元色素濃度は25～250μMであることが好ましく、また、キシロース等の活性酸素発生源濃度は0.2～2重量%程度であることが好ましい。

【0017】本発明においては、具体的にはNBTを含むリン酸緩衝液中に、図1に示す如く、金属試料電極1A～1Cと照合電極2を浸漬し、両電極間に電位差計5等を接続し、その後、水中にキシロースを添加混合し、電位差を測定する。この場合、金属試料電極が複数ある場合には、図1に示す如く、一定の時間間隔で各金属試料電極の電位を測定するように、電極切換装置4で電位差計5の切換を行う。

【0018】水中にキシロースを添加すると、キシロースから活性酸素が発生し、この活性酸素が還元される過程で金属試料電極面から電子が引き抜かれる結果、腐食が進行すると共に、この腐食の進行が電位上昇として測定される。

【0019】従って、金属試料電極1A～1Cと照合電極2との間の自然電位の変化を測定することにより、金属試料電極を構成する金属材料の耐腐食性を評価することができる。

【0020】本発明において、金属試料電極としては、通常の熱交換器用ないし配管用金属材料よりなるもの、具体的には銅又は鋼材よりなる半割管材を用いて、これらの耐腐食性を電位変化として容易に評価することができる。

【0021】なお、照合電極としてはAg-AgCl電極等を用いることができ、本発明において、金属試料電極及び照合電極を浸漬させる試験水の水量としては、1リットル程度の小容量で十分足りる。

【0022】

【作用】微生物の関与したSUS、銅等の金属材料の孔食の前段階として、自然電位の上昇がみられることはよく知られているが、本発明者らは、この電位上昇が微生物の関与により金属表面に活性酸素が生成することによりもたらされると考察した。即ち、金属材料は、系内の活性酸素が水にまで還元される過程で、電子が金属面から引き抜かれる結果、腐食が進行するものと考察した。そして、少量の活性酸素を発生する実際の微生物反応による腐食を模擬すべく、活性酸素発生源により水中で微量の活性酸素を発生させると共に、酸化還元色素を電子キャリア又は電子メディエータとして反応に介在させ、金属試料電極の金属材料から電子を引き抜き易い環境とした試験水中に、金属試料電極と照合電極とを浸漬し、両電極間の自然電位の変化を測定する。これにより、金属試料電極の金属材料の耐腐食性を、適度に加速された電位変化として、迅速かつ正確に評価することができる。

【0023】なお、NBT等の酸化還元色素は、活性酸素発生源と金属試料電極表面との間の電子の授受を円滑にする電子キャリア又は電子メディエータとしての役割

を果たしているものと推定され、この酸化還元色素が存在しないと、活性酸素量が少な過ぎて、反応が円滑に進行しなくなる。

【0024】

【実施例】以下に実施例を挙げて本発明をより具体的に説明する。

【0025】なお、以下において、活性酸素発生源としてはキシロースを、また、酸化還元色素としてはNBTを用い、図1に示す試験装置で実施した。

【0026】実施例1

まず、KH₂PO₄（分子量136）、Na₂HPO₄（分子量142）の各0.015M溶液を混合してpH8.1のリン酸緩衝液を調製した。NBT40mgをこの0.015Mリン酸緩衝液（pH8.1）1リットルに溶解して、50μMのNBTを含むリン酸緩衝液（pH8.1）を調製した。

【0027】このNBTリン酸緩衝液中に、表面の加工状態の異なる下記銅製テストピースNo. 1～3と照合電極（Ag-AgCl電極）とを浸漬し、37℃に維持した。これにキシロースを1重量%濃度となるように添加して、電位の経時変化を測定し、図2の結果を得た。

【0028】テストピースNo. 1：半割燐脱酸銅管（表面未加工）の外側をシリコン樹脂で被覆した、外径15.88mm、肉厚0.5mm、未加工内表面積10cm²のテストピース

テストピースNo. 2：テストピースNo. 1の内表面に溝深さ0.15mmの溝を平行間隔（0.33mm）に設けたもの

テストピースNo. 3：テストピースNo. 1で用いたと同様の半割燐脱酸銅管の内面をシリコン樹脂で被覆し、平滑な外表面を利用したもの

比較のために従来法によるテストも行った。即ち、試験水100リットルにテストピースNo. 1、2とAg-AgCl電極とを浸漬し、電位の経日変化を測定し、図3の結果を得た。

【0029】図2、3より、本発明によれば、従来法による電位上昇を短時間で再現できることが明らかである。

【0030】

【発明の効果】以上詳述した通り、本発明の耐腐食性の試験方法によれば、小容量の試験水中に、金属試料電極と照合電極とを浸漬して、両電極間の電位差を測定するのみで、短時間で容易に金属試料電極の金属材料の耐腐食性を適正に評価することができる。

【0031】因みに、本発明の方法によれば、多数の金属試料電極を用いる場合であっても、用いる試験水水量は約1リットル程度の小容量で良く、また、試験時間も数時間程度で良く、試験水容量及び試験時間は、従来のモニタリング方法に比べて大幅に低減される。しかも、H₂O₂を発生させる従来の耐微生物腐食試験に比べ

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て、実際の腐食状況をより適正に模擬することができるため、より正確な評価を行える。

【図面の簡単な説明】

【図1】本発明の耐腐食性の試験方法の実施に好適な試験装置の一実施例を示す系統図である。

【図2】実施例1における測定結果（本発明方法による）を示すグラフである。

【図3】実施例1における測定結果（従来法による）を示すグラフである。

示すグラフである。

【符号の説明】

1A, 1B, 1C 金属試料電極

2 照合電極

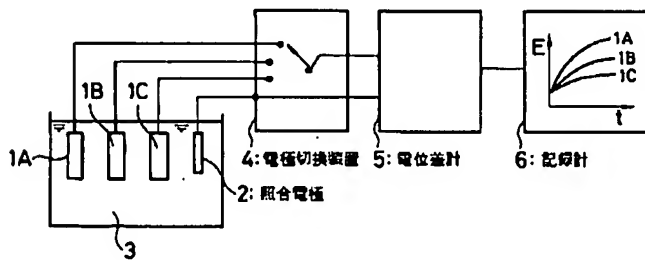
3 活性酸素発生源と酸化還元色素を含む水

4 電極切換装置

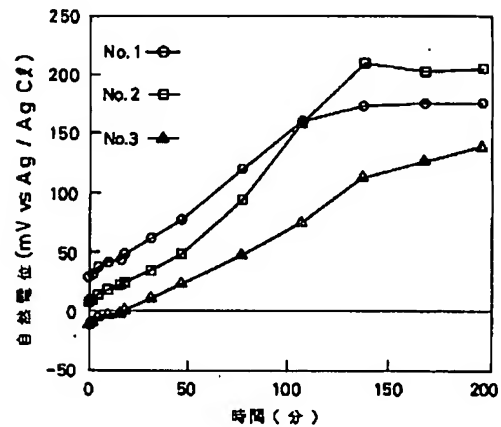
5 電位差計

6 記録計

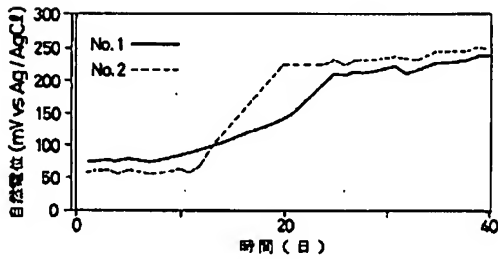
【図1】



【図2】



【図3】



PATENT ABSTRACTS OF JAPAN

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(71)Applicant : **KURITA WATER IND LTD**

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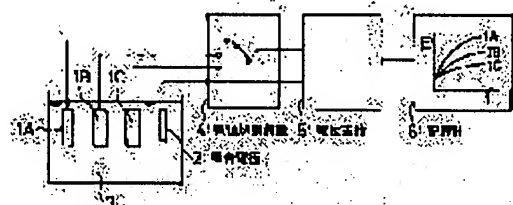
(54) TEST METHOD FOR ANTI-CORROSION CHARACTERISTIC

(57)Abstract:

PURPOSE: To correctly evaluate corrosion of a metal material with easily in a short time with small quantity of test water by soaking a metal material electrode and a collate electrode in the water containing active oxygen generating source and oxidation reduction pigment.

CONSTITUTION: Metal sample electrodes 1A, 1B and 1C and a collate electrode 2 are soaked in water 3 containing active oxygen generating source and oxidation reduction pigment. And, a potential difference meter 5 which measures the potential difference between the electrodes 1A, 1B and 1C and the collate electrode 2 is connected through an electrode switching device 4. A recorder 6 displays the measurement result by the potential difference meter 5. As an active oxygen

generating source, xylose which is easy to generate active oxygen through automatic oxidation reaction in water, etc., are used. When the xylose is added to the water, the active oxygen is generated, and, in the process where the active oxygen is reduced, electron is taken out of the metal sample, as a result, corrosion advances, so that it is measured as potential rising. Thus, based an potential changes between the metal sample electrodes 1A-1C and collate electrode 2, anti-corrosion characteristic of metal material is evaluated.



LEGAL STATUS

[Date of request for examination]

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[Date of final disposal for application]

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[Date of registration]

[Number of appeal against examiner's decision of rejection]

[Date of requesting appeal against examiner's decision of rejection]

[Date of extinction of right]

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CLAIMS

[Claim(s)]

[Claim 1] The test method of the corrosion resistance characterized by immersing a metal sample electrode and a reference electrode in underwater [containing an active oxygen generation source and oxidation reduction coloring matter], and measuring the potential difference between two electrodes.

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DETAILED DESCRIPTION

[Detailed Description of the Invention]

[0001]

[Industrial Application] This invention relates to the test method of corrosion resistance, and relates to the test method of the corrosion resistance which evaluates especially the corrosion of the object for heat exchangers thru/or the metallic material for piping, and pitting of the copper tube with which a microorganism especially involves by easy equipment quickly and proper.

[0002]

[Description of the Prior Art] Since the unexpected situations, such as a shutdown of a plant, may be produced when localized corrosion advances in piping used for piping, a heat exchanger, etc. and the increase of the pitting depth and it result in penetration, the technique of foreknowing generating of localized corrosion, i.e., pitting, is searched for.

[0003] Conventionally, generating of a heat exchanger or pitting of piping stopped operation of the facility concerned and water flow, sampled the part, and foreknew it by investigating the pitting situation of a sample.

[0004] However, by such approach, since it must destroy in order to stop operation of a facility and to sample the part, there is a fault of affecting operation of works. And there is also a fault that great time amount, an effort, and costs will start before a measurement result comes out.

[0005] There is the approach of acting as the monitor of the advance situation of pitting of piping to solve such a fault. That is, it acts as the monitor of the pitting situation by dipping the test piece which consists of the same quality of the material as piping which carries out monitoring to underwater [which was extracted from the inside of a system drainage system, or a system drainage system], for example, and measuring aging of the potential difference between this test piece and reference electrode. This approach is made possible [presuming pitting by un-destroying], without using for piping the phenomenon in which the rest potential of a tubing material rises as a preceding paragraph story which pitting generates, and stopping operation of a facility according to such an approach.

[0006] on the other hand -- "the collection of corrosion corrosion prevention symposium summaries" of May 25, 1994 issue -- a glucose is decomposed into 129th page - the 132nd page by oxidizing enzyme, and a hydrogen peroxide (H₂ O₂) is generated in it -- making -- H₂ O₂ The method of performing the bacterial corrosion-proof trial of steel materials using the reaction which receives an electron from steel materials and is set to H₂ O is proposed.

[0007]

[Problem(s) to be Solved by the Invention] Using the rise phenomenon of the rest potential of the above-mentioned tubing material, a test piece needs to be immersed from the inside of a system drainage system, or a system drainage system into the water extracted in the large quantity (about 100l.), and it is necessary to measure the variation per day of the potential by the approach of acting as the monitor of the advance situation of pitting using a test piece. Since the daily measurement for about one month is needed in order to judge the existence of a potential rise by this approach, it is a short time of several hours, and, moreover, there is a fault that it cannot evaluate with the trial water of small capacity.

[0008] On the other hand, there are the following troubles in the bacterial corrosion-proof test method of the steel materials indicated by "the collection of corrosion corrosion prevention symposium summaries." Namely, a lot of H₂ O₂ Since it is accelerated aging which makes it generate, it is high-concentration H₂ O₂. It acts on direct steel materials and a potential rise is brought about. By such system, a problem remains as a trial examination of the bacterial corrosion (however, subsequent advance is quick once reaction starts.) reaction for which the test atmosphere is too excessive and a reaction advances gradually over a long period of time.

[0009] This invention solves the above-mentioned conventional trouble, and it aims at offering the test method of the corrosion resistance which can, easy moreover, evaluate the corrosion of the object for heat exchangers thru/or the metallic material for piping, especially pitting of the copper tube with which a microorganism involves proper with the trial water of small capacity in a short time.

[0010]

[Means for Solving the Problem] The test method of the corrosion resistance of this invention is immersed in underwater [containing an active oxygen generation source and oxidation reduction coloring matter] in a metal sample electrode and a reference electrode, and is characterized by measuring the potential difference between two electrodes.

[0011] This invention is explained with reference to a drawing below at a detail.

[0012] Drawing 1 is the schematic diagram showing one example of the suitable testing device for operation of the test method of the corrosion resistance of this invention. For a metal sample electrode and 2, 1A, 1B, and 1C are the inside of drawing, and water ("trial water" may be called below) which is a reference electrode and contains an active oxygen generation source and oxidation reduction coloring matter. While being immersed into three, the potentiometer 5 for measuring the potential difference between these metal sample electrodes 1A, 1B, and 1C and a reference electrode 2 is connected through the electrode switching unit 4. Moreover, the recorder 6 which displays the measurement result of this potentiometer 5 is formed.

[0013] In this invention, although it is easy to generate active oxygen by the autoxidation reaction underwater and an available xylose (xylose) is moreover easily used suitably as an active oxygen generation source, it is not limited to this at all.

[0014] On the other hand, as oxidation reduction coloring matter, NBT (Nitro Blue Tetrazolium:C₄₀H₃₀N₁₀O₆ Cl₂ = molecular weight 817.65) is suitable.

[0015] Preferably, 20 degrees C or more, although it is added by constant temperature and the water especially maintained by 30 degrees C or more preferably and a trial is presented with these active oxygen generation source and oxidation reduction coloring matter As this water, from the ability of the rise of the measured value of the potential difference to be made remarkable It is desirable to use the phosphate buffer solution containing a phosphoric acid or phosphate, and the neutrality which is especially 100-1000 ppm thru/or fine alkalinity, i.e., a with a pH of about six to nine phosphate buffer solution, are suitable the Lynn concentration of 100 ppm or more especially.

[0016] As for oxidation reduction coloring matter concentration, such as NBT in such a phosphate buffer solution, it is desirable that it is 25-250microM, and, as for active oxygen generation source concentration, such as a xylose, it is desirable that it is about 0.2 - 2 % of the weight.

[0017] In this invention, in the phosphate buffer solution which specifically contains NBT, as shown in drawing 1 , the metal sample electrodes 1A-1C and a reference electrode 2 are immersed, potentiometer 5 grade is connected between two electrodes, addition mixing of the xylose is carried out underwater after that, and the potential difference is measured. In this case, when there are two or more metal sample electrodes, as shown in drawing 1 , a potentiometer 5 is switched with the electrode switching unit 4 so that the potential of each metal sample electrode may be measured with a fixed time interval.

[0018] If a xylose is added underwater, active oxygen occurs from a xylose, and as a result of drawing out an electron from a metal sample electrode side in the process in which this active oxygen is returned, while corrosion advances, advance of this corrosion will be measured as a potential rise.

[0019] Therefore, the corrosion resistance of the metallic material which constitutes a metal sample electrode can be evaluated by measuring change of the rest potential between the metal sample

electrodes 1A-1C and a reference electrode 2.

[0020] In this invention, such corrosion resistance can be easily evaluated as potential change as a metal sample electrode using what consists of the usual object for heat exchangers thru/or the usual metallic material for piping, and the half-segmented tubing material which specifically consists of copper or steel materials.

[0021] In addition, an Ag-AgCl electrode etc. can be used as a reference electrode, and the small capacity of about 1l. is sufficient enough in this invention as amount of water of the trial water in which a metal sample electrode and a reference electrode are made immersed.

[0022]

[Function] Although it was well known as a preceding paragraph story of pitting of metallic materials, such as SUS, copper, etc. with which the microorganism involved, that the rise of rest potential will be seen, this invention persons considered that this potential rise was brought about when active oxygen generates to a surface of metal by the intervention of a microorganism. That is, in the process in which the active oxygen in a system is returned even to water, the metallic material was considered to be that to which corrosion advances, as a result of drawing out an electron from a metal side. And that the corrosion by the actual microorganism reaction which generates a small amount of active oxygen should be simulated, while generating the active oxygen of a minute amount underwater by the active oxygen generation source, a reaction is made to intervene by making oxidation reduction coloring matter into an electronic carrier or an electronic mediator, a metal sample electrode and a reference electrode are immersed in the trial underwater made into the environment which is easy to draw out an electron from the metallic material of a metal sample electrode, and change of the rest potential between two electrodes is measured. Thereby, the corrosion resistance of the metallic material of a metal sample electrode can be evaluated quickly and correctly as potential change accelerated moderately.

[0023] In addition, unless oxidation reduction coloring matter, such as NBT, is presumed to be what has played a role of the electronic carrier which makes smooth transfer of the electron between an active oxygen generation source and a metal sample electrode front face, or an electronic mediator and this oxidation reduction coloring matter exists, there will be too few amounts of active oxygen, and a reaction will not advance smoothly.

[0024]

[Example] An example is given to below and this invention is more concretely explained to it.

[0025] In addition, the xylose was used as an active oxygen generation source, and NBT was used for below as oxidation reduction coloring matter, and it carried out with the testing device shown in drawing 1.

[0026] an example 1 -- first -- every of KH_2PO_4 (molecular weight 136) and Na_2HPO_4 (molecular weight 142) -- 0.015M solution was mixed and the phosphate buffer solution of pH8.1 was prepared. NBT40mg was dissolved in 1l. (pH8.1) of this 0.015M phosphate buffer solution, and the phosphate buffer solution (pH8.1) containing NBT of 50microM was prepared.

[0027] In this NBT phosphate buffer solution, it was immersed and following copper test piece No.1-3 and the reference electrode (Ag-AgCl electrode) with which surface processing conditions differ were maintained at 37 degrees C. To this, the xylose was added so that it might become concentration 1% of the weight, aging of potential was measured, and the result of drawing 2 was obtained.

[0028] the outside of test piece No.1:half-segmented phosphorus-deoxidized-copper tubing (a front face -- raw) was covered with silicon resin -- It is 2 the outer diameter of 15.88mm, the thickness of 0.5mm, and 10cm of raw internal-surface products. Test piece test piece No.2 : [Thing test piece No. which established the slot with a channel depth of 0.15mm in parallel spacing (0.33mm) at the internal surface of test piece No.1] 3: The inside of the same half-segmented phosphorus-deoxidized-copper tubing was covered with silicon resin with having used by test piece No.1, and the test by the conventional method was also performed for the thing comparison using a smooth outside surface. That is, test piece No.1, 2, and an Ag-AgCl electrode were immersed in 100l. of trial water, the variation per day of potential was measured, and the result of drawing 3 was obtained.

[0029] According to this invention, it is clearer than drawing 2 and 3 that the potential rise by the

conventional method is reproducible in a short time.

[0030]

[Effect of the Invention] According to the test method of the corrosion resistance of this invention, a metal sample electrode and a reference electrode can be immersed in the trial underwater of small capacity, and the corrosion resistance of the metallic material of a metal sample electrode can be easily evaluated in a short time proper only by measuring the potential difference between two electrodes as explained in full detail above.

[0031] the trial water incidentally used even if it is the case where many metal sample electrodes are used according to the approach of this invention -- about 1l. in small capacity is sufficient as amount of water, and test time is also good in about several hours, and trial struk capacity and test time are sharply reduced compared with the conventional monitoring approach. And H2 O2 Since an actual corrosion situation can be simulated more proper compared with the conventional bacterial corrosion-proof trial to generate, more exact evaluation can be performed.

[Translation done.]

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TECHNICAL FIELD

[Industrial Application] This invention relates to the test method of corrosion resistance, and relates to the test method of the corrosion resistance which evaluates especially the corrosion of the object for heat exchangers thru/or the metallic material for piping, and pitting of the copper tube with which a microorganism especially involves by easy equipment quickly and proper.

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PRIOR ART

[Description of the Prior Art] Since the unexpected situations, such as a shutdown of a plant, may be produced when localized corrosion advances in piping used for piping, a heat exchanger, etc. and the increase of the pitting depth and it result in penetration, the technique of foreknowing generating of localized corrosion, i.e., pitting, is searched for.

[0003] Conventionally, generating of a heat exchanger or pitting of piping stopped operation of the facility concerned and water flow, sampled the part, and foreknew it by investigating the pitting situation of a sample.

[0004] However, by such approach, since it must destroy in order to stop operation of a facility and to sample the part, there is a fault of affecting operation of works. And there is also a fault that great time amount, an effort, and costs will start before a measurement result comes out.

[0005] There is the approach of acting as the monitor of the advance situation of pitting of piping to solve such a fault. That is, it acts as the monitor of the pitting situation by dipping the test piece which consists of the same quality of the material as piping which carries out monitoring to underwater [which was extracted from the inside of a system drainage system, or a system drainage system], for example, and measuring aging of the potential difference between this test piece and reference electrode. This approach is made possible [presuming pitting by un-destroying], without using for piping the phenomenon in which the rest potential of a tubing material rises as a preceding paragraph story which pitting generates, and stopping operation of a facility according to such an approach.

[0006] on the other hand -- "the collection of corrosion corrosion prevention symposium summaries" of May 25, 1994 issue -- a glucose is decomposed into 129th page - the 132nd page by oxidizing enzyme, and a hydrogen peroxide (H₂ O₂) is generated in it -- making -- H₂ O₂ The method of performing the bacterial corrosion-proof trial of steel materials using the reaction which receives an electron from steel materials and is set to H₂ O is proposed.

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EFFECT OF THE INVENTION

[Effect of the Invention] According to the test method of the corrosion resistance of this invention, a metal sample electrode and a reference electrode can be immersed in the trial underwater of small capacity, and the corrosion resistance of the metallic material of a metal sample electrode can be easily evaluated in a short time proper only by measuring the potential difference between two electrodes as explained in full detail above.

[0031] the trial water incidentally used even if it is the case where many metal sample electrodes are used according to the approach of this invention -- about 1l. in small capacity is sufficient as amount of water, and test time is also good in about several hours, and trial struk capacity and test time are sharply reduced compared with the conventional monitoring approach. And H2 O2 Since an actual corrosion situation can be simulated more proper compared with the conventional bacterial corrosion-proof trial to generate, more exact evaluation can be performed.

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TECHNICAL PROBLEM

[Problem(s) to be Solved by the Invention] Using the rise phenomenon of the rest potential of the above-mentioned tubing material, a test piece needs to be immersed from the inside of a system drainage system, or a system drainage system into the water extracted in the large quantity (about 100l.), and it is necessary to measure the variation per day of the potential by the approach of acting as the monitor of the advance situation of pitting using a test piece. Since the daily measurement for about one month is needed in order to judge the existence of a potential rise by this approach, it is a short time of several hours, and, moreover, there is a fault that it cannot evaluate with the trial water of small capacity.

[0008] On the other hand, there are the following troubles in the bacterial corrosion-proof test method of the steel materials indicated by "the collection of corrosion corrosion prevention symposium summaries." Namely, a lot of H₂ O₂ Since it is accelerated aging which makes it generate, it is high-concentration H₂ O₂. It acts on direct steel materials and a potential rise is brought about. By such system, a problem remains as a trial examination of the bacterial corrosion (however, subsequent advance is quick once reaction starts.) reaction for which the test atmosphere is too excessive and a reaction advances gradually over a long period of time.

[0009] This invention solves the above-mentioned conventional trouble, and it aims at offering the test method of the corrosion resistance which can, easy moreover, evaluate the corrosion of the object for heat exchangers thru/or the metallic material for piping, especially pitting of the copper tube with which a microorganism involves proper with the trial water of small capacity in a short time.

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MEANS

[Means for Solving the Problem] The test method of the corrosion resistance of this invention is immersed in underwater [containing an active oxygen generation source and oxidation reduction coloring matter] in a metal sample electrode and a reference electrode, and is characterized by measuring the potential difference between two electrodes.

[0011] This invention is explained with reference to a drawing below at a detail.

[0012] Drawing 1 is the schematic diagram showing one example of the suitable testing device for operation of the test method of the corrosion resistance of this invention. For a metal sample electrode and 2, 1A, 1B, and 1C are the inside of drawing, and water ("trial water" may be called below) which is a reference electrode and contains an active oxygen generation source and oxidation reduction coloring matter. While being immersed into three, the potentiometer 5 for measuring the potential difference between these metal sample electrodes 1A, 1B, and 1C and a reference electrode 2 is connected through the electrode switching unit 4. Moreover, the recorder 6 which displays the measurement result of this potentiometer 5 is formed.

[0013] In this invention, although it is easy to generate active oxygen by the autoxidation reaction underwater and an available xylose (xylose) is moreover easily used suitably as an active oxygen generation source, it is not limited to this at all.

[0014] On the other hand, as oxidation reduction coloring matter, NBT (Nitro Blue Tetrazolium: $C_{40}H_{30}N_{10}O_6 Cl_2$ = molecular weight 817.65) is suitable.

[0015] Preferably, 20 degrees C or more, although it is added by constant temperature and the water especially maintained by 30 degrees C or more preferably and a trial is presented with these active oxygen generation source and oxidation reduction coloring matter As this water, from the ability of the rise of the measured value of the potential difference to be made remarkable It is desirable to use the phosphate buffer solution containing a phosphoric acid or phosphate, and the neutrality which is especially 100-1000 ppm thru/or fine alkalinity, i.e., a with a pH of about six to nine phosphate buffer solution, are suitable the Lynn concentration of 100 ppm or more especially.

[0016] As for oxidation reduction coloring matter concentration, such as NBT in such a phosphate buffer solution, it is desirable that it is 25-250microM, and, as for active oxygen generation source concentration, such as a xylose, it is desirable that it is about 0.2 - 2 % of the weight.

[0017] In this invention, in the phosphate buffer solution which specifically contains NBT, as shown in drawing 1 , the metal sample electrodes 1A-1C and a reference electrode 2 are immersed, potentiometer 5 grade is connected between two electrodes, addition mixing of the xylose is carried out underwater after that, and the potential difference is measured. In this case, when there are two or more metal sample electrodes, as shown in drawing 1 , a potentiometer 5 is switched with the electrode switching unit 4 so that the potential of each metal sample electrode may be measured with a fixed time interval.

[0018] If a xylose is added underwater, active oxygen occurs from a xylose, and as a result of drawing out an electron from a metal sample electrode side in the process in which this active oxygen is returned, while corrosion advances, advance of this corrosion will be measured as a potential rise.

[0019] Therefore, the corrosion resistance of the metallic material which constitutes a metal sample

electrode can be evaluated by measuring change of the rest potential between the metal sample electrodes 1A-1C and a reference electrode 2.

[0020] In this invention, such corrosion resistance can be easily evaluated as potential change as a metal sample electrode using what consists of the usual object for heat exchangers thru/or the usual metallic material for piping, and the half-segmented tubing material which specifically consists of copper or steel materials.

[0021] In addition, an Ag-AgCl electrode etc. can be used as a reference electrode, and the small capacity of about 1l. is sufficient enough in this invention as amount of water of the trial water in which a metal sample electrode and a reference electrode are made immersed.

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OPERATION

[Function] Although it was well known as a preceding paragraph story of pitting of metallic materials, such as SUS, copper, etc. with which the microorganism involved, that the rise of rest potential will be seen, this invention persons considered that this potential rise was brought about when active oxygen generates to a surface of metal by the intervention of a microorganism. That is, in the process in which the active oxygen in a system is returned even to water, the metallic material was considered to be that to which corrosion advances, as a result of drawing out an electron from a metal side. And that the corrosion by the actual microorganism reaction which generates a small amount of active oxygen should be simulated, while generating the active oxygen of a minute amount underwater by the active oxygen generation source, a reaction is made to intervene by making oxidation reduction coloring matter into an electronic carrier or an electronic mediator, a metal sample electrode and a reference electrode are immersed in the trial underwater made into the environment which is easy to draw out an electron from the metallic material of a metal sample electrode, and change of the rest potential between two electrodes is measured. Thereby, the corrosion resistance of the metallic material of a metal sample electrode can be evaluated quickly and correctly as potential change accelerated moderately.

[0023] In addition, unless oxidation reduction coloring matter, such as NBT, is presumed to be what has played a role of the electronic carrier which makes smooth transfer of the electron between an active oxygen generation source and a metal sample electrode front face, or an electronic mediator and this oxidation reduction coloring matter exists, there will be too few amounts of active oxygen, and a reaction will not advance smoothly.

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EXAMPLE

[Example] An example is given to below and this invention is more concretely explained to it.

[0025] In addition, the xylose was used as an active oxygen generation source, and NBT was used for below as oxidation reduction coloring matter, and it carried out with the testing device shown in drawing 1.

[0026] an example 1 -- first -- every of KH_2PO_4 (molecular weight 136) and Na_2HPO_4 (molecular weight 142) -- 0.015M solution was mixed and the phosphate buffer solution of pH8.1 was prepared. NBT40mg was dissolved in 1l. (pH8.1) of this 0.015M phosphate buffer solution, and the phosphate buffer solution (pH8.1) containing NBT of 50microM was prepared.

[0027] In this NBT phosphate buffer solution, it was immersed and following copper test piece No.1-3 and the reference electrode (Ag-AgCl electrode) with which surface processing conditions differ were maintained at 37 degrees C. To this, the xylose was added so that it might become concentration 1% of the weight, aging of potential was measured, and the result of drawing 2 was obtained.

[0028] the outside of test piece No.1 :half-segmented phosphorus-deoxidized-copper tubing (a front face -- raw) was covered with silicon resin -- It is 2 the outer diameter of 15.88mm, the thickness of 0.5mm, and 10cm of raw internal-surface products. Test piece test piece No.2 : [Thing test piece No. which established the slot with a channel depth of 0.15mm in parallel spacing (0.33mm) at the internal surface of test piece No.1] 3: The inside of the same half-segmented phosphorus-deoxidized-copper tubing was covered with silicon resin with having used by test piece No.1, and the test by the conventional method was also performed for the thing comparison using a smooth outside surface. That is, test piece No.1, 2, and an Ag-AgCl electrode were immersed in 100l. of trial water, the variation per day of potential was measured, and the result of drawing 3 was obtained.

[0029] According to this invention, it is clearer than drawing 2 and 3 that the potential rise by the conventional method is reproducible in a short time.

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DESCRIPTION OF DRAWINGS

[Brief Description of the Drawings]

[Drawing 1] It is the schematic diagram showing one example of the suitable testing device for operation of the test method of the corrosion resistance of this invention.

[Drawing 2] It is the graph which shows the measurement result (based on this invention approach) in an example 1.

[Drawing 3] It is the graph which shows the measurement result (based on a conventional method) in an example 1.

[Description of Notations]

1A, 1B, 1C Metal sample electrode

2 Reference Electrode

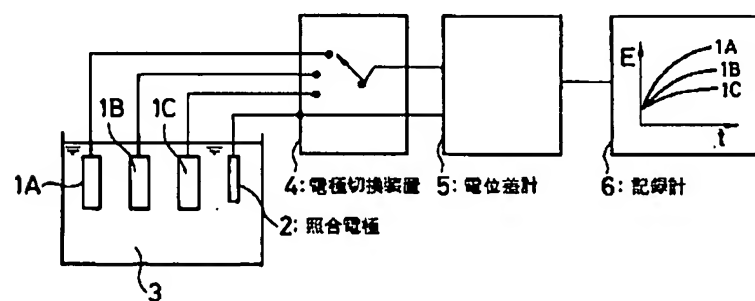
3 Water Containing Active Oxygen Source of Release and Oxidation Reduction Coloring Matter

4 Electrode Switching Unit

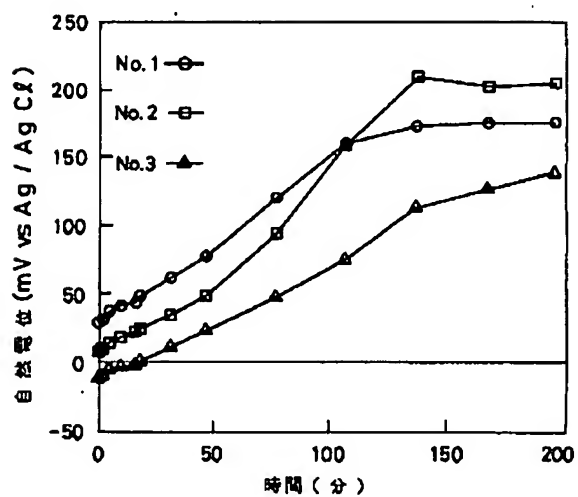
5 Potentiometer

6 Recorder

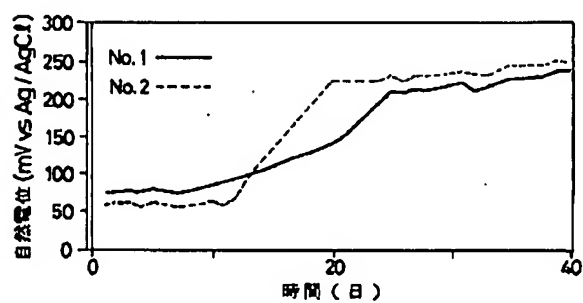
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